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Non-stationary luminescence as a probe of charged species

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Abstract

We have developed a new approach – non-stationary luminescence (NsL), for probing charged species in irradiated solids. This original two-stage technique is based on some kind of "pump-probe" experiments with controlled *in situ* "injection" of electrons via their release from the traps stimulated by the sample heating. The ionic species of interest are first generated by an intense electron beam. The species produced are then probed by recombination luminescence under low-density beam to minimize production of new charged species. The "probing" – detection of NsL spectra, is performed under gradual heating of the irradiated sample in order to release electrons from progressively deeper traps and initiate the recombination with positively charged species. The approach developed is demonstrated by examples D_2-doped solid Xe and solid N_2.

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Keywords: nonstationary luminescence; activation spectroscopy; neutralization reactions; charged species

1. Introduction

Detection of charged centers in solids by luminescence is a nontrivial task. Luminescence spectra reflect final states of electronic excitation i.e. one detects the final products of relaxation processes in particular neutral species as products of neutralization reaction. Wherein information on primary charged reactants is appeared to be lost. Although a long, 90-year history of solid nitrogen spectroscopy, starting from Vegard (1924) the role of charged species was recognized only recently. So accumulation of electrons in pre-irradiated solid nitrogen was registered using thermally stimulated exoelectron emission TSEE by Khyzhniy et al. (2010), emission of electrons was also detected upon heating of nitrogen-containing Impurity-He condensates by Boltnev et al. (2013). Production of ionic

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species N_3^+ in the electron-bombarded solid nitrogen was revealed using IR and UV absorption measurements by Wu et al. (2013). Ionic centers $(N_2)_2^+$ were suggested to contribute to the post-desorption observed upon heating of a pre-irradiated solid N_2 Savchenko (2013). Generally accepted way to probe charged species is thermally stimulated luminescence TSL Vij (1998). When the solid is exposed to ionizing radiation, electron-hole pairs are produced. Some of charge carries (electrons/holes) are inevitably stabilized in the traps of various depths, and remain there once irradiation is completed. We will discuss the case when electrons are the trapped carriers. These electrons can be released either by gradual heating of the sample or by irradiating it by photons of an appropriate energy. Detrapped electrons are detected as TSEE or thermally stimulated current TSC or indirectly detected via the appearance of TSL resulting from neutralization reactions. It is worth noting that at higher temperatures also atoms and small radicals may start to diffuse through the solid and recombine resulting in TSL. Molecule emissions observed in this case will represent transitions with dissociative limit corresponding atoms in the ground state. It is obvious from this that measurements of the total yield of TSL give no way to distinguish neutral and charge recombination processes. More informative are measurements of spectrally resolved TSL in particular detection of panchromatic curves.

Here we present a new approach to probe charged centers in solids – non-stationary luminescence. This two-stage technique is to some extent combination of cathodoluminescence CL and spectrally resolved TSL. The charged centers are first generated by an intense electron beam. The ionic species produced are then probed by recombination luminescence which is induced by low-density electron beam under gradual heating. As this takes place electrons released from the increasingly deeper traps recombine with positively charged species contributing to the NsL spectra. We applied this technique to model objects of insulating materials – solidified gases. As examples two systems are considered – solid Xe doped with D_2 and solid N_2.

2. Experimental section

2.1. Sample preparation

The experiments were performed using facilities at TUM and ILT. In both cases films of solidified gases (pure nitrogen and D_2-doped solid Xe) were grown from the gas phase by deposition onto a cold metal substrate mounted in a high-vacuum chamber with a base pressure of 10^{-8} mbar. The gas-handling system and vacuum chamber were degassed by heating under pumping before each experiment. Premix with a predetermined dopant concentration was prepared in the gas-handling system at room temperature. In these experiments we used 0,1% D_2 admixture. The substrate was cooled by a liquid He cryostat (at ILT) or a closed-cycle 2-stage Leybold RGD 580 cryostat (at TUM). High-purity (99.999%) gases were used. Deuterium isotopic enrichment was 99,8%. The presence of impurities in the samples was controlled by the luminescence spectra. The structure of samples and therefore charge trap levels and their distribution within the energy gap were varied by changing the deposition temperature and gas flow rate. The gas flow rate during deposition was controlled by means of a Brokhorst Gas Flow Controller. The sample thickness was determined by observing the pressure decrease in a known volume of the gas-handling system. The typical deposition rate was about 10^{-1} μms^{-1}. The substrate temperature controlled with a Si diode can be set as needed. The samples were of a high optical quality and looked transparent. The experiments were performed in the temperature range 5-35 K with α-phase N_2 and 6-65 K with D_2-doped Xe matrix.

2.2. Charged centers generation

To ionize samples and dissociate D_2 molecules we used an electron beam in dc regime. An advantage of the electron beam use is an effective ionization of samples – the ionization cross sections at irradiation by an electron beam are by a factor of 10^2 greater than those of photoionization. Moreover, the samples can be probed in depth by changing the beam energy and doing so one could discriminate between radiation-induced processes in the bulk and those on its surface. The use of low-energy electrons allows irradiating the samples in sub-threshold mode to avoid the knock-on defect formation and sputtering. The threshold electron beam energy is about 1 keV for N_2 and 10 keV for Xe. Taking this into account the N_2 samples were irradiated by a 0,5 keV electron beam and 1 keV Xe matrix. For all samples irradiation was performed at 6 K to populate shallow traps. The current density can be set from

7 μAcm^{-2} to 7 $mAcm^{-2}$. The beam was focused so as to provide irradiation of the sample over the entire area. The sample temperature was monitored during the whole experiment. The radiation dose was varied by an exposure time. The cathodoluminescence CL spectra measurements over the range from 200 nm to 1100 nm were performed using a CCD-based Ocean Optics S2000 spectrometer (at TUM). At ILT the CL spectra were detected concurrently in the visible range and in vacuum ultraviolet VUV with two spectrometers. To monitor excited species formation and accumulation of radiation-induced centers the dose dependences were measured recording the luminescence spectra sequences or, alternatively, recording luminescence intensity at the selected wavelength.

2.3. Non-stationary luminescence technique

The suggested non-stationary luminescence technique is aimed to reveal charged species in irradiated solids. To be specific, as it was mentioned above we consider the case when the mobile charge carriers are electrons. As long as the electrons produced under irradiation are trapped in the lattice at some defect sites, positively charged ionic species survived fast recombination remain stable at low temperatures. The main idea of the NsL method is to pinpoint a contribution of neutralization reactions to CL spectra. For the purpose the charged species of interest were first generated with an intense electron beam of a high current density. In different experiments we used current densities from 0,1 $mAcm^{-2}$ up to 1 $mAcm^{-2}$. Temperature of samples was carefully controlled to avoid considerable heating. As a rule the temperature growth under beam did not exceed 0,3 K. Duration of exposure was set on the approach of corresponding emission to saturation. Usually this time was about 10 min and large enough to fill the electron traps available. Then the ionic species generated were probed by NsL which was induced by a low-density electron beam under gradual heating. The controlled heating was performed at a constant rate of 6 $Kmin^{-1}$. An intensity of probing electron beam was set by an order of magnitude lower than that at charge centers generation to minimize the production of new ions. Electrons released from the progressively deeper traps recombine with positively charged species contributing to the NsL spectra. This contribution to the NsL spectrum results in non-monotonic temperature evolution of the spectrum intensity, which is defined by trap levels structure. Upon reversing the temperature change to cooling, the intensity of NsL remains nearly constant.

2.4. Charged centers probing by activation spectroscopy

In order to make sure that features of the NsL spectra stem from neutralization reactions we used activation spectroscopy methods. As demonstrated by Savchenko and Bondybey (2005), the use of current activation spectroscopy methods along with traditional TSL is of service for distinguishing reactions of charged and neutral species. Taking into account the observation by Khyzhniy et al. (2010) TSEE from pre-irradiated solid N_2 and by Khyzhniy et al. (2009) TSEE from solid Xe we employed measurement of TSEE and TSL detected at the same wavelength as the NsL. Measurements were carried out in the visible, near UV and VUV ranges. In view of the high sensitivity of TSEE and TSL upon the sample structure, impurity concentration and sample prehistory, there is clear need to perform time correlated measurements of both thermally stimulated phenomena on the same sample to get reliable results and come to solid conclusions. TSEE current was detected with an electrode kept at a small positive potential +9 V and connected to the current amplifier. When measuring the relaxation emissions we used the same heating mode and rate as in the experiments on NsL, viz. heating at a constant rate of 6 $Kmin^{-1}$. The entire control of the experiment and the simultaneous acquisition of the TSL and TSEE yields, as well as recording the sample temperature were accomplished using a computer program developed specifically for these studies.

3. Non-stationary luminescence study

3.1. Formation of Xe_2D^+ *centers*

Noble-gas hydride molecules and ions attracted considerable interest in physical and chemical studies Bondybey (1999), Gerber (2004), Grochala et al. (2011). More often the experiments were performed using the UV photolysis of molecular species containing an electronegative fragment (HCl, HF, HBr etc.) in noble-gas matrices. Besides HNgY (Y=F, Cl, Br, I) species $(Ng_2H)^+$ and their deuterated analogues were created and detected by infrared (IR)

spectroscopy. The absorption of the cations decayed at low temperatures and enhanced as the temperature increased. This process shows a strong isotope effect. Example of such a behavior was recently demonstrated by Lignell et al. (2010). This behavior has stimulated much interest to the question on stability of ionic species $(Ng_2H)^+$ and $(Ng_2D)^+$. Several mechanisms of their decay were proposed. Beyer et al. (1999) suggested that the room-temperature black-body radiation induced diffusion of protons and deuterons. A dominant contribution of tunneling into the diffusion was supposed by Beyer et al. (2003) analyzing the rate constants for an elementary step of the diffusion of H^+ and D^+. Another process, which is liable to be responsible for the decay of Ng_2H^+ and Ng_2D^+ ionic centers in the noble-gas matrices, is their neutralization by electrons. Such a possibility was considered by Khriachtchev et al. (2005). It was supposed that the mechanism of neutralization involves tunneling of an electron from an electronegative fragment or another trap to the $(Ar_2H)^+$ center. Neutralization of Xe_2H^+ by electrons released from traps was detected by Savchenko et al. (2010) in the experiments performed on solid Xe doped with H_2 without any admixture of electronegative species. It was the first attempt to apply the method of non-stationary luminescence to probe Ng_2H^+ species. An emission of the neutralization reaction product – $(Xe_2H)^*$ was detected at 252 nm.

Here we present the results on NsL of deuterated species $(Xe_2D)^*$. The luminescence spectra of solid Xe doped with D_2 were excited with an electron beam as described in section 2.2 and detected at 7 K. Their transformation with an exposure time is shown in Fig. 1 in the range of the emission band at 253 nm which stems from the radiative transition of the $(Xe_2D)^*$ to a repulsive part of the ground state. A pronounced enhancement of the band under exposure to a high-density electron beam was observed, pointing to the efficient dissociation of D_2 and formation of the noble-gas hydride molecule.

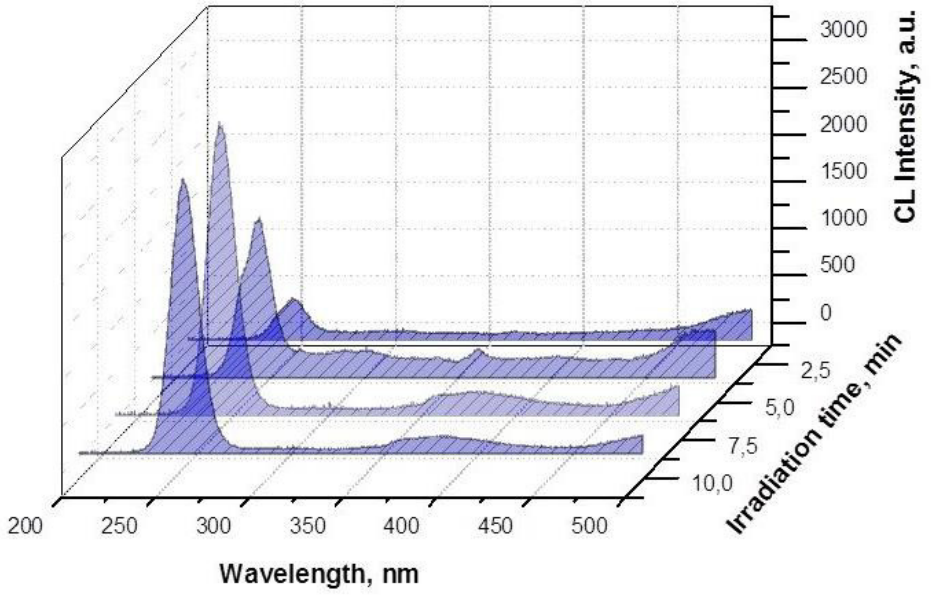

Fig. 1. Transformation of the $(Xe_2D)^*$ emission band with exposure time.

Growth of the $(Xe_2D)^*$-band intensity is supposed to be due to accumulation of $(Xe_2D)^+$ centers, followed by their neutralization. In order to check possible contribution from the neutralization reaction:

$$(Xe_2D)^+ + e^- \rightarrow Xe_2D^* \rightarrow h\nu_1 + Xe + Xe + D + \Delta E \qquad (1)$$

at the second stage of the NsL experiment, the ionic species $(Xe_2D)^+$ were probed by the procedure, described in section 2.3 using a low-density electron beam. The “probing” which was carried out on gradual linear heating of the

sample constitutes in fact controlled *in situ* "injection" of electrons into the Xe matrix via their successive release from the traps. Being promoted to the conduction band electrons then recombine with the ionic centers $(Xe_2D)^+$ by reaction (1) resulting in the $(Xe_2D)^*$ emission. Fig. 2 demonstrates the evolution of the Xe_2D^* emission band upon heating.

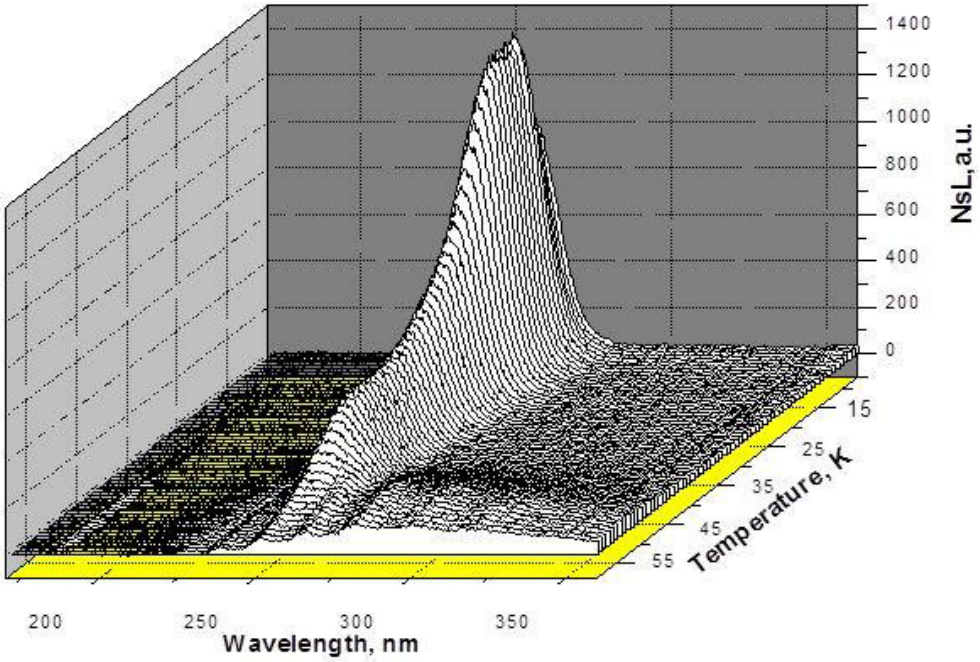

Fig. 2. NsL in the range of $(Xe_2D)^*$ emission measured under low-density electron beam at the sample heating.

The spectra were recorded successively every 10 s. As seen in the Fig. 2, the intensity of the NsL band shows a non-monotonic behavior – it first increases rapidly while heating, reaching a maximum in the range 10-15 K, and then decreases yielding however weak shoulder at about 40 K. Upon reversing the temperature change, not shown in the Figure, the NsL intensity has been retained with no modification indicating bleaching of the ionic centers $(Xe_2D)^+$ by previous processing (heating). The stability of ionic centers with respect to neutralization is determined by the efficiency of electron detrapping and electron transport. The mobility of electrons in solid Xe is a few thousand $cm^2V^{-1}s^{-1}$, higher than those in other noble-gas solids as pointed by Song and Williams (1996).

It is instructive to consider the NsL behavior as compared to the thermally stimulated emission of electrons TSEE from Xe matrix. In view of positive electron affinity – 0.5 eV by Song and Williams (1996), there is a barrier for electrons to escape. However an uncompensated negative space charge accumulation during irradiation of the sample by electron beam facilitates overcoming the barrier as shown by Savchenko et al. (2012). As this takes place one might expect the temperature dependence of the NsL intensity to "correlate" with peaks of TSEE due to the "internal electron emission". The yield of TSEE from Xe matrix was measured after irradiation of the sample in the regime identical to that used in the NsL experiment. Comparison of the TSEE yield with the NsL temperature dependence is shown in Fig. 3. The temperature behavior of the $(Xe_2D)^*$ emission in NsL measured under the low-density electron beam clearly correlates with the yield of TSEE measured after identical pre-irradiation of the sample. Note that a position of the main low-temperature maximum in the system with deuterated species appeared to be close to that found in the NsL of hydrogenated species by Savchenko et al. (2010) pointing that defects of Xe matrix as electron traps are a source of electrons driving the neutralization reaction.

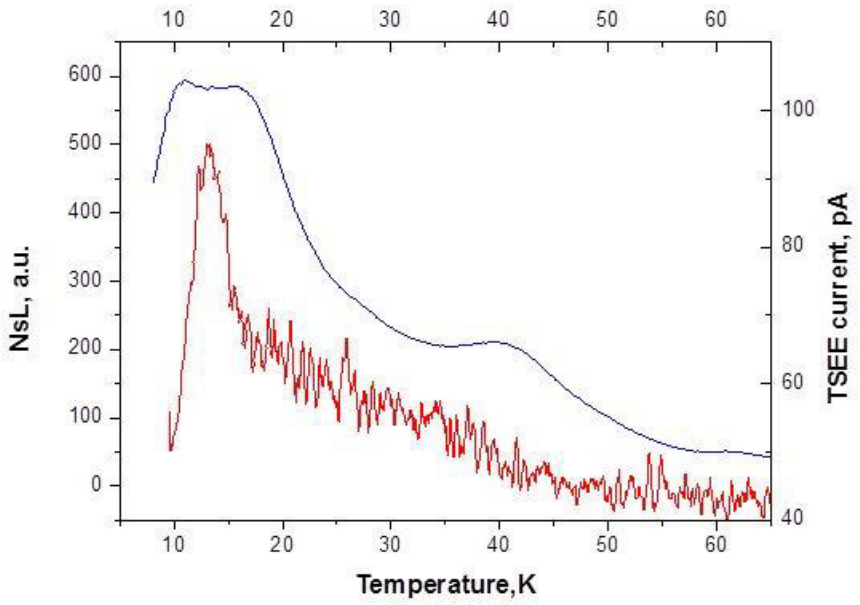

Fig. 3. Comparison of the $(Xe_2D)^*$ emission band temperature behaviour with the TSEE yield taken from the pre-irradiated sample.

3.2. Fingerprints of N_4^+ *species*

High interest to formation of N_4^+ species is related to the problem of creating high energy density materials Nguyen (2003), Zarko (2010) and References therein. In earlier studies $^{14}N_4^+$ and $^{15}N_4^+$ cations were detected in Ne matrix using the ESR technique by Knight (1987) and IR absorption by Thompson and Jacox (1990). According to the data on photoionized afterglow plasmas presented by Cao and Johnsen (1991) neutralization of N_4^+ species proceeds via the dissociative recombination reaction and results in the appearance of excited nitrogen molecule in the $C^3\Pi_u$ state:

$$N_4^+ + e^- \rightarrow N_2^* + N_2 \rightarrow h\nu_2 + N_2 + N_2 + \Delta E_2 \qquad (2)$$

Based on the study of spectrally resolved TSL performed by Savchenko et al. (2014) reaction (2) was suggested to be a source of energy for the desorption of nitrogen molecules in electronically excited state.

To demonstrate the capability of NsL method we applied this technique also to study of charged species in solid N_2 irradiated by an electron beam. The cathodoluminescence CL spectrum of solid N_2 in the range of second positive system (the $C^3\Pi_u \rightarrow B^3\Pi_g$ transition) is presented in Fig. 4a. The features detected coincide with those registered in Savchenko et al. (2014). "Hot" luminescence – transitions from excited vibrational states (up to $v'=2$), emerged in the spectrum. The distinctive characteristic of the features observed is their coincidence with those observed under excitation of the gas-phase spectra. This coincidence is explained by the fact that the desorbing nitrogen molecules are in the excited state, in other words, because the desorbing excited molecules emit photons already being in the gas phase. Intensity of the second positive system increased with the exposure time and then saturated indicating accumulation of radiation-induced centers responsible for the emissions of excited N_2^* molecules. These centers are most likely to be ionic centers N_4^+ – initial "reactants" of the neutralization reaction (2). The dose dependence of the $C^3\Pi_u \rightarrow B^3\Pi_g$ transition in cathodoluminescence is shown in Fig. 4b for an example (0-1) band.

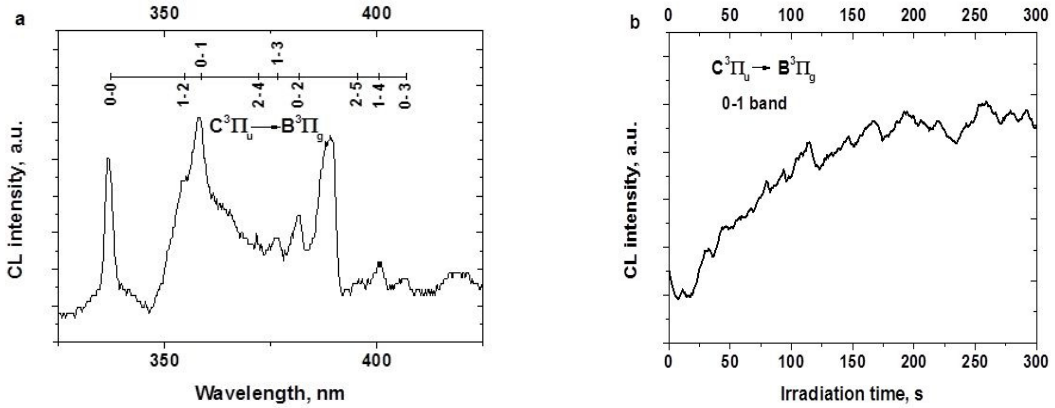

Fig. 4. (a) The second positive system in CL of solid N_2; (b) Dose dependence of the second positive system (0-1 band).

Two nitrogen samples were grown and irradiated with an electron beam at identical conditions as described in section 2.3. Then on one sample the temperature dependence of NsL was measured at the wavelength of the $C^3\Pi_u(v'=0)\rightarrow B^3\Pi_g(v''=1)$ transition under "gentle" irradiation. TSL was measured at the same wavelength on another sample at the same mode of heating. Also was concurrently measured the yield of TSEE. Comparison of the corresponding curves is shown in Fig. 5.

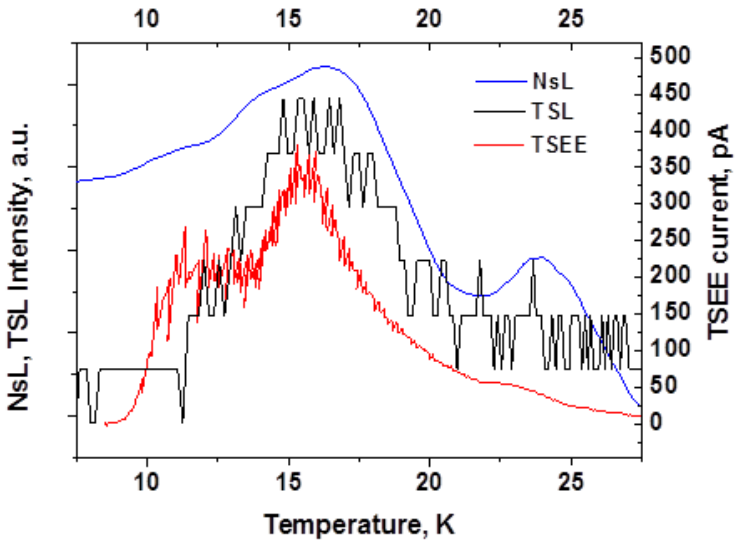

Fig. 5. Yields of the NsL and TSL measured in 0-1 band of the second positive system and yield of TSEE.

Features of optical and current yields correlate indicating common process underlying the phenomena – the neutralization reaction (2). Note that the coincidence of TSL and TSEE maxima is not a surprise because of the absence of a barrier for electrons to escape due to negative electron affinity of solid nitrogen Bader et al. (1984).

4. Summary

A new approach – non-stationary luminescence (NsL), have been developed to probe charged species in irradiated solids. The method presents combination of CL and TSL. At first stage charged centers are generated by an intense electron beam. The ionic species produced are then probed by measuring NsL under gradual heating. At this stage a low-density beam is used to minimize production of new charged species. Herewith electrons are released from progressively deeper traps and recombine with positively charged species. Features of the temperature behavior of NsL are determined by the spectrum of trap levels. Comparison of NsL taken from D_2-doped solid Xe and solid N_2 with TSEE and TSL from the identical samples demonstrates that the suggested NsL method is well suited for probing ionic species in irradiated solids.

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